

## THE CHANGING NATURE OF DEPOSITS FORMED DURING THERMAL STRESSING OF JET FUELS

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### ABSTRACT

A JP-5 fuel was subjected to thermal stress at various temperatures in a flow tube with a wire stretched along its length. The deposits formed on the wire, as well as those collected on a filter were examined by field ionization mass spectrometry. Two distinct kinds of spectra were observed. The first had a picket-fence like appearance and the masses corresponded to long chain alkanes. The spectrum spanned a mass range from about 300 to 500 Da. The alkanes in the fuel have molecular weights ranging from about 130 to 240. These waxy deposits were formed possibly by the coupling of alkyl radicals. The second class of deposits is characterized with a very rich spectrum spanning a mass range from 200 to 800 Da. Evidently, this deposit is formed by the reaction of many different fuel components and not just the alkanes. FT-IR examination of this deposit showed a strong peak due to aromatic C-H stretch. Implications of these two kinds of deposits to the overall thermal instability of jet fuels will be discussed.

### INTRODUCTION

The fuel in an aircraft is subjected to much thermal stress, and in advanced aircraft the degree of thermal stress is only expected to increase. This stress often results in the formation of insolubles that end up depositing on engine parts, fuel lines, and nozzles. In some instances, the deposits at critical points can completely block the flow of fuel to the engine with disastrous consequences. Not surprisingly, therefore, the thermal stability of jet fuels has been the subject of many studies, and jet fuels must pass the JFTOT test for thermal stability before they are deemed acceptable.

In pioneering work, Hazlett demonstrated the importance of autoxidation process in deposit formation during thermal stressing of fuels.<sup>1</sup> This process involves generation of radical species, which initiate a chain reaction with oxygen to give hydroperoxides, which are then considered to react with minor fuel components, that likely contain nitrogen and/or sulfur, to produce insoluble deposits. A substantial amount of work has been performed to elucidate the mechanisms of deposit formation, and many details have been added to this picture; however the essential aspects of this theory have been validated.<sup>2</sup>

A number of attempts have also been made to model the deposit formation. The models often treat all deposits as a lumped component, and proceed to describe the build up as a function of thermal stress (time, temperature).<sup>3</sup> Simple Arrhenius behavior is often assumed, although there is evidence that the observed activation energy in systems at low temperatures (long time) tends to be significantly lower than that observed at high temperatures (short time).<sup>4</sup> This behavior is clearly indicative of a change in the mechanism, and it should be reflected in the models, if they are to correctly describe the phenomena.

In this paper we show that the chemical nature of the deposits at lower and higher temperatures is markedly different. This finding is in concert with the varying activation energies, and might provide a basis for building a more accurate model.

## EXPERIMENTAL

A JP 5 fuel was flowed through a heated, glass-lined, stainless tube (1/8" OD, 0.7" ID, 44" long) at 0.5 mL/min. A stainless steel wire (0.008" dia) was stretched along the center of the tube, and some of the deposits were collected on this wire. The effluent passed through a stainless steel filter (0.2  $\mu$ m) where the insolubles were collected. The effluent fuel cools before reaching the filter, and so the deposits on the wire represent materials that are insoluble in the hot fuel, whereas those on the filter are of materials insoluble in the fuel at the lower temperature of the filter. The wire deposits and the filtered deposits were analyzed by an Fourier transform infrared (FTIR) spectrometer and a field ionization mass spectrometer (FIMS).

## RESULTS AND DISCUSSION

FIMS analysis of the fuel showed the molecular weight of the component species ranged from about 120 to 230 Da, with an average value of about 170 Da. The spectrum also shows components with whole range of unsaturation indices, as would be expected of a typical fuel. The FIMS of the deposits collected on the wire and the filter at 150°C are shown in Figure 1. These spectra are characterized by a picket-fence like appearance. The prominent peaks are 14 Da apart and centered around 340 Da. The masses correspond to acyclic alkanes ( $14n + 2$ ), although they could also be due to acyclic ketones. These components are expected to arise from the autoxidation of alkanes. The long-chain waxy products are dimers resulting from the coupling of the alkyl and alkoxy radicals are not likely to be very soluble in the fuel and therefore it is not surprising that they drop out of the solution most readily. The filter deposits collected at 150°C show a very similar spectrum. The amount of the filter deposit was considerably larger, and consequently, the spectrum is less noisy. The filter deposit also shows peaks corresponding to dimers formed by the coupling of species other than acyclic alkanes.

Figure 2 shows the analogous spectra collected at 450°C. Although the amount of the wire deposit collected was larger at the higher temperature, its spectrum—and hence its nature—is essentially the same as that collected at 150°C. In contrast, the spectrum of the filter deposit is very rich, and shows a broad distribution of masses ranging from about 180 to over 800 Da. The waxes seen in the wire deposit are also present, but they are overshadowed by the other components.

FIMS analysis of the deposits clearly shows that the thermal deposits fall into two classes. The first are the alkane-rich waxes, which tend to be more insoluble, plate out even when the fuel is hot. These deposits do not contain much heteroatoms, except for some oxygen. The other class consists of a wide range of compounds, possibly with a much higher heteroatom content. This class of compounds forms later in the sequence, it is more soluble, and precipitates out when the fuel is somewhat cooler. The waxy deposits could also absorb the other fuel components and in effect increase their residence time in the hot zone. If that case, we would expect the rate of deposit formation to increase with time. Indeed, that was observed by Kamin and coworkers<sup>5</sup> when they monitored the deposit formation in a JFTOT with a fiber optic monitor. A preliminary model that incorporates the two different classes of deposits was able to mimic this time dependent variation in the rate of deposit formation.

## REFERENCES

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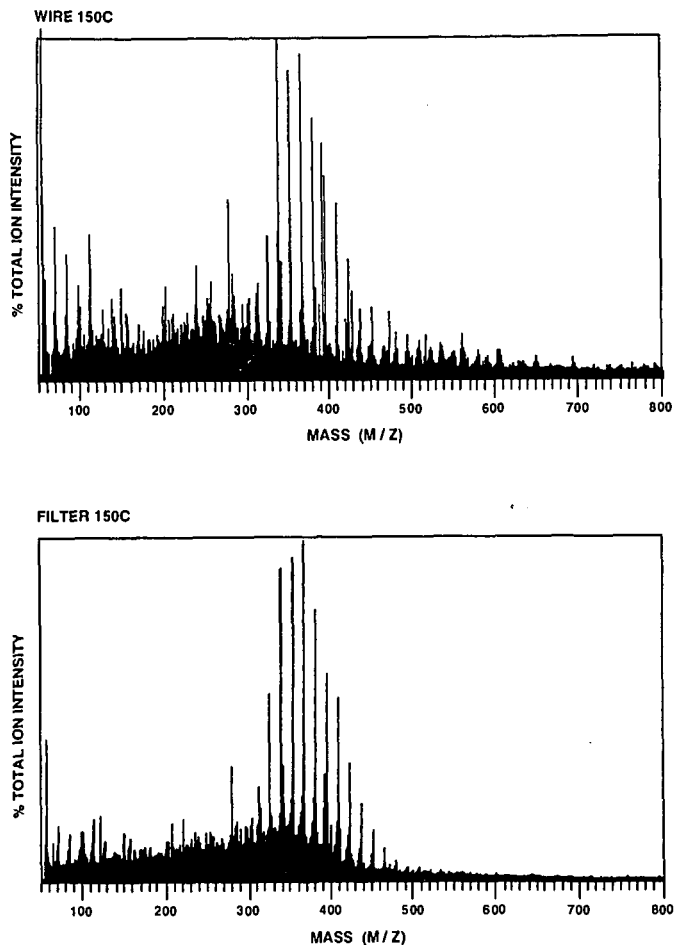


Figure 1. Field ionization mass spectrum of deposits collected on (a) wire and (b) filter from thermal stressing of aerated JP5 at 150°C.

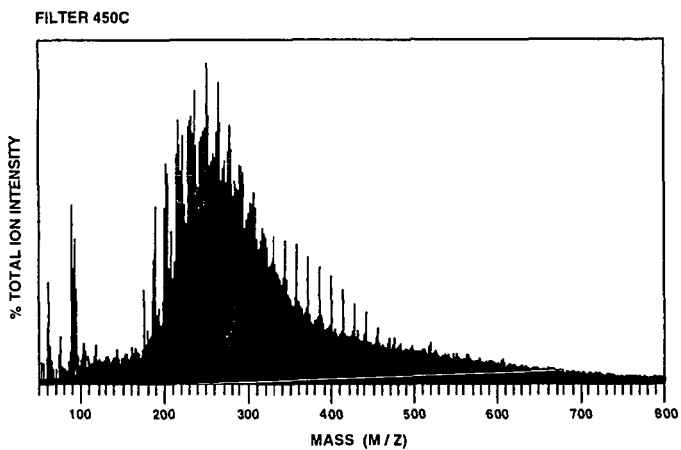
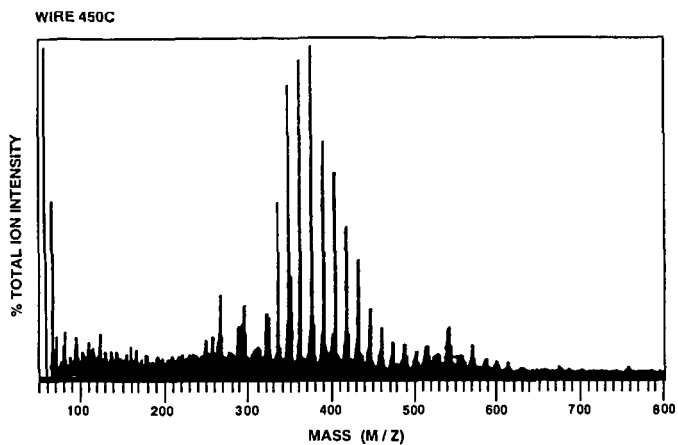


Figure 2. Field ionization mass spectrum of deposits collected on (a) wire and (b) filter from thermal stressing of aerated JP5 at 450°C.